Photoelectrochemical Conversion of Solar Energy Tween 60 – Bromocresol Purple

Ascorbic acid system in photogalvanic cell

K.R. Genwa*,C.P. Sagar

Department of Chemistry
Jai Narain Vyas University
Jodhpur, India
krg2004@rediffmail.com

***Abstract*-In the present work, solar energy conversion into electrical energy studied by use of photogalvanic cell. A photogalvanic cell is a device which absorb light photons with in a highly absorbing electrolyte and electrical power is generated by subsequent charge transfer to the electrolyte by redox reactions. This cell works on the photogalvanic effect. In this article photogalvanic effect was studied in photogalvanic cell consisting Tween 60 - Bromocresol purple - Ascorbic acid system. The Bromocresol purple photosensitized the reaction in solution. The photo potential, photocurrent and power generated in cell were 811.0 mV, 65.0 µA and 34.16 mW, respectively. The cell performance (storage capacity) was 150 min. in dark. Conversion efficiency and fill factor calculated as 0.328% and 0.38, respectively. The effect of other parameters like pH, light intensity, diffusion length, electrode area and temperature on cell electrical outputs were investigated in detail and finally mechanism for the generation of the photocurrent has also been proposed.**

Keywords-Tween 60; Bromocresol purple; ascorbic acid; conversion efficiency

NOMENCLATURE

i_{max}	Maximum photocurrent
i_{eq}	Equilibrium photocurrent
V_{oc}	Open circuit Voltage
i_{sc}	Short circuit current
V_{pp}	Potential at the power point
i_{pp}	Current at the power point
ff	Fill factor
D_L	Diffusion length
$t_{1/2}$	Storage capacity

I. INTRODUCTION

The increasing energy demand in the near future will force us to seek environmentally clean alternative energy resources. The emergence of nanomaterials as the new building blocks to construct light energy harvesting assemblies has opened up new ways to utilize renewable energy sources. Although renewable energy such as solar radiation is ideal to meet the projected demand, it requires new initiatives to harvest incident photons with greater efficiency (Baranham et al., 2006).

The first generation photovoltaic devices suffer from high cost of manufacturing and installation. The second generation devices consisting of CuInGaSe2 (CIGS) polycrystalline semiconductor thin films can bring down the price significantly, but their efficiency needs to be enhanced in order to make them practically viable. The third generation devices that can deliver high efficiency devices at an economically viable cost and ability to design nanostructured semiconductors, organic-inorganic hybrid assemblies, and molecular assemblies opens up new ways to design such third generation light energy conversion devices (Kamat, 2007). Dye- sensitized solar cells have stabilized themselves as a potential low cost alternative to conventional solar cell owing to there remarkably high power conversion efficiency combined with low-tech fabrication processes (Durr et al.; 2005). Belinicher and Sturman (1980) reported the photogalvanic effect in the regions of impurity, interband, and interband light absorption. Later on this work get momentum by work of other coworkers time to time (Albery et al.;1979, Memming;1980, Amata et al.;1990, Fan et al.;1982, Alfredo et al.;1990, Kaneko and Wohrle;1991, Mukhopadhyay and Bhowmik; 1992, Mackay; 2004, Mayer; 2005, Madhwani et al.; 2007, Jahanshah et al.; 2009,). Lal (2007) used mixed dyes in photogalvanic cell, Gangotri and Bhimwal (2011) studied the performance of photogalvanic cell, Gangotri an Indora (2010) studied in mix reductant and Gangotri and Gangotri (2010) have studies of micellar effect and comparative studies in three dyes. Recently, our research group reported reasonable values of electrical out put with different dyes as photosensitizer in photogalvanic cell in presence of surfactants (Genwa et al.; 2006, Genwa and Chouhan; 2006, Genwa and Genwa; 2008, Genwa and Kumar; 2009).

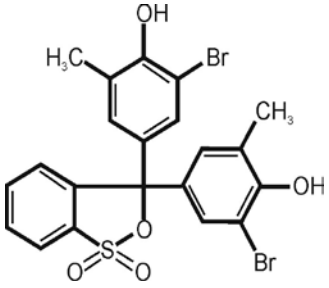
In view of review of literature, it was observed that no attention has been paid to increase overall efficiency to gain the commercial viability of the photogalvanic cells. Therefore, the present system Tween 60 - Bromocresol purple – Ascorbic acid is undertaken in the photogalvanic cell for solar energy conversion and storage.

II. MATERIALS AND METHOD

A. Materials

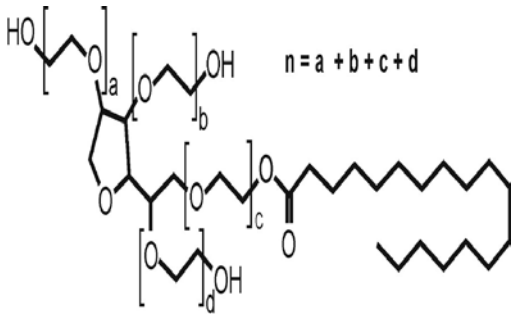
1) Bromocresol Purple：

Slightly yellow power, insoluble in water but soluble in Ethanol, Molecular formula - $C_{21}H_{16}Br_2O_5S$, Molecular weight – 540.24, Maximum absorption (λmax) – 580 nm .



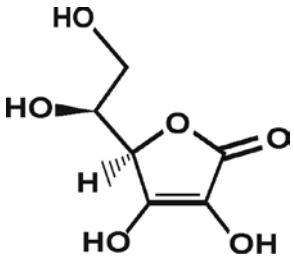
2) Tween 60 (Polyoxyethylene Sorbitan Monostearate) :

A pale yellow semisolid liquid, Soluble in water, molecular formula – $C_{24}H_{46}O_6(C_2H_4O)n$, Molecular weight – 1312.



3) Ascorbic Acid (Vitamin C):

White to slightly yellowish crystalline power, Soluble in water, Molecular formula $C_6H_8O_6$ and Molecular weight 176.13



B. Method

Bromocresol purple (Loba Chemie), Tween 60 (LDH), Ascorbic acid (SISCO) and NaOH (RANKEM) solution having concentration $1.6x10^{-5}$ M, $1.2x10^{-3}$ M, $2.0x10^{-3}$ M and 1.0 N respectively were used in present work. Photogalvanic effect of dye was studied using H- shaped glass tube which consist known amount of the solution of Bromocresol purple, Tween 60, Ascorbic acid, NaOH solution and water so as to keep total volume of the mixture always 25.0 ml. A Platinum electrode (1.0x1.0 cm^2) was dipped in one limb and a Saturated Calomel Electrode (SCE) is immersed in another limb of the H- tube. The terminals of the electrodes were then connected to a digital pH meter and the whole cell is placed in dark. The potential was measured in dark when the cell attains a stable potential. The limb containing platinum electrode was focused to the light source. A tungsten lamp of 200W was used as light source which having the intensity 10.4 mW/cm^2 at the surface of the cell. The incident intensity of light measured in the laboratory with the help of Solar intensity meter- Solarimeter Model 501CEL (Surya, Ahamadabad). A water filter placed between the illuminated chamber and the light source to cut off thermal radiations. Photo potential and photocurrent were measured by digital pH meter (Systonics 335) and digital ammeter (Osaw). Absorption spectra were recorded using Systonics Spectrophotometer 106 with the matched pair of silica cuvetts (path length 1cm). All spectral measurements were duplicated in a constant temperature water bath maintained with in $\pm 1\ ^0C$ and mean values were processed for data analysis.

III. MECHANISM

Light energy is converted in to chemical energy by driving a suitable redox reaction against the potential gradient. The thionine-Fe (II) aqueous photogalvanic system was studies by Jana (2000). Reactions are as follow:

$$TH+ \xrightarrow{h\upsilon} {}^1TH+ \longrightarrow {}^3TH+$$

$${}^3TH^+ + H+ \longrightarrow 3TH_2^{2+}$$

$${}^3TH_2^{2+} \longrightarrow TH^+(I_{se} \text{ to ground state})$$

$${}^3TH2^{2+} + Fe^{2+} \longrightarrow {*}TH_2^+ + Fe^{3+}$$

(Semi – thionine radical formation)

$${*}TH_2^+ + Fe^{3+} \longrightarrow TH^+ + Fe^{2+} + H^+$$

(Back thermal reaction)

$${*}TH_2^+ + TH_2^+ \rightleftharpoons TH^+ + TH_3^+$$

(Dispropotionation reaction)

$${*}TH_2^+ \longrightarrow TH^+ + H^+ + e^-$$

(Anode Reaction at illuminated electrode)

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

(Dark electrode)

Where TH^+ was represented dark thione is the oxidized form.

On the basis of above, the tentative reaction mechanism in our system proposed as:

A. Illuminated Chamber

On irradiation, dye molecule get excited

$$\text{Dye} \xrightarrow{h\upsilon} \text{Dye*} \quad (1)$$

Ground state first excited state

$$\text{Dye*} + R \longrightarrow \text{Dye}^-(\text{semi or luco}) + R^+ \quad (2)$$

Triplet state

The excited dye molecule accept an electron from reductant and convert into semi or luco form of dye, and the reductant into its excited state form.

B. At platinum Electrode

The semi or luco form of dye loses an electron and converted into original dye molecule

$$Dye^- \longrightarrow Dye + e^- \quad (3)$$

Dark chamber

- At counter electrode

$$Dye + e^- \longrightarrow Dye^- \text{ (semi or luco)} \quad (4)$$

Finally luco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule and the cycle will go on

$$Dye^- + R^+ \longrightarrow Dye + R \quad (5)$$

Where Dye, Dye^-, R and R^+ represents the dye, reduced form of dye, reductant and oxidized form of reductant respectively.

IV. RESULTS AND DISCUSSION

A Effect of Variation of Dye (Bromocresol Purple), Surfactant (Tween 60), and Reductant (Ascorbic Acid) Concentration

Results showing the effect of dye, surfactant and reductant concentration are given in Table 1. It was observed that the photo potential and photocurrent of Tween 60 - Bromocresol purple – Ascorbic acid system for the better performance of the photogalvanic cell proper concentration of dye needed. Experimentally, photo potential and photocurrent increased with increase in concentration of the Bromocresol purple. A maxima was obtained at certain dye concentration. On further increasing dye concentration, a decrease in the electrical output was observed. On the lower concentration range of dye, there are limited numbers of dye molecules to absorb the major portion of the light in the path and therefore, there was minimum electrical output. A maximum photocurrent (130 µA) and photo potential (811.0 mV) was generated at an optimum value of dye concentration ($1.6x10^{-5}$ M).

The neutral surfactant Tween 60 was used to study effect of surfactant on cell outputs. It was observed that photo potential and photocurrent were increased on increasing the concentration of Tween 60. A maxima was obtained at a certain value and then decreased on further increase in surfactant concentration. The most important properties of miceller systems are the ability to solubilize a variety of molecules and substantial catalytic effect on chemical reaction.

With the increase in concentration of the reductant photo potential and photocurrent was found to increase to maximum value at $2.0x10^{-3}$ M and then electrical output decreased because fever reductant molecule were available for electron donation to photosensitizer (Dye) molecule. Higher concentration of reductant again resulted to decrease in electrical output due to the large numbers of reductant molecules hinder the dye molecule from reaching electrode in the desired time limit.

B Effect of Variation of pH

The electrical output of the photogalvanic cell was affected by the variation of pH. It was observed that the system was quite sensitive to pH of the solution. The photo potential and photocurrent were increased with increase pH value (in alkaline range) of the cell. At pH 10.18, a maxima was obtained. On further increase in pH, photo potential and photocurrent were decreased.

It was also observed that the pH for the optimum condition has a relation with pKa of the reductant, and the desired pH is higher than in pKa value (pH>pKa). The reason may be the availability of the reductant in its cationic form, which is a better donor form. The results showing the effect of pH are summarized in Table 2.

C *Effect of Diffusion Length and Electrode Area*

Effect of variation of diffusion length on the current parameters of the cell (i_{max}, i_{eq}) initial rate of generation of photocurrent are studied using H-Shaped cell of different diameters. i_{max} found to increase with diffusion length. It was observed that in the first few minutes of illumination there is sharp increase in the photocurrent. The conductivity of electro active species depends on its population between electrodes. As diffusion length increased, the volume of dye solution and intern population of dye molecule (Bromocresol purple) increased leading higher i_{max} the electroactive nature of dye/dye- is provide by the fact that i_{max} increase with diffusion length. Therefore it may be concluded that the main electro active species are the leuco or semi form of dye- and the dye in the illumination and the dark chamber respectively. The reductant its oxidation products act only as electron carriers in the path. The results are summarized in Table 3. The effects of variation of electrode area on the current parameters of the cell were also studied. Experimentally, it was observed that with increase electrode area the value of maximum photocurrent (i_{max}) was found to increase. The results are summarized in Table 4.

D Effect of Variation of Light Intensity

The intensity of light was also affects the electrical output of the cell. This effect was observed by using solar intensity meter. It was observed that photocurrent showed a linear increasing behavior with the increase in light intensity whereas photo potential increase in logarithmic manner. This was due to increase in number of photons per unit area (incident power) striking the dye molecules and the platinum electrode. The dependence of light intensity on photopotential and photocurrent of the cell are graphically represented in Fig 1.

E Current – Voltage (I-V) Characteristics

Open circuit voltage (V_{oc}) and short circuit current (i_{sc}) of the photogalvanic cell were measured under the continuous illumination of light, with the help of digital pH meter (keeping the circuit open) and a micro ammeter (keeping the circuit closed), respectively. The external parameters (photopotential and photocurrent) of the photogalvanic cell in between this two extreme values (V_{pp} and i_{pp}) were recorded with the help of a carbon pot (log 407K) connected in the circuit of micro ammeter, through which an external load applied. i-V curve of the cell containing Tween 60 - Bromocresol purple – Ascorbic acid system is shown in Fig. 2. It was seen that i-V curve deviated from its regular rectangular shape. A point in i-V curve, called power point (pp), was determined where the product of current and potential was maximum and fill-factor was calculated as 0.38 using formula:

$$\text{Fill-factor (ff)} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \qquad (6)$$

F Storage Capacity (Performance) and Conversion Efficiency of the Cell

The performance was determined in term of $t_{1/2}$ i.e. the time required in fall of the power output to its half at power point in dark. It was observed that the cell can be used in dark for 150 minutes (Fig.3) in Tween 60 - Bromocresol purple – Ascorbic acid system in photogalvanic cell. The conversion efficiency of the cell was determined as 0.32% using formula:

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{A \times 10.4\ \text{mWcm}^{-2}} \times 100\% \qquad (7)$$

G Absorption Properties of Bromocresol Purple – Tween 60

The spectral properties of Bromocresol purple dye was studied with the help of spectrophotometer. The dye observed absorption intensity (λmax) in visible region with maximum at 580 nm. Maximum absorption is recorded at

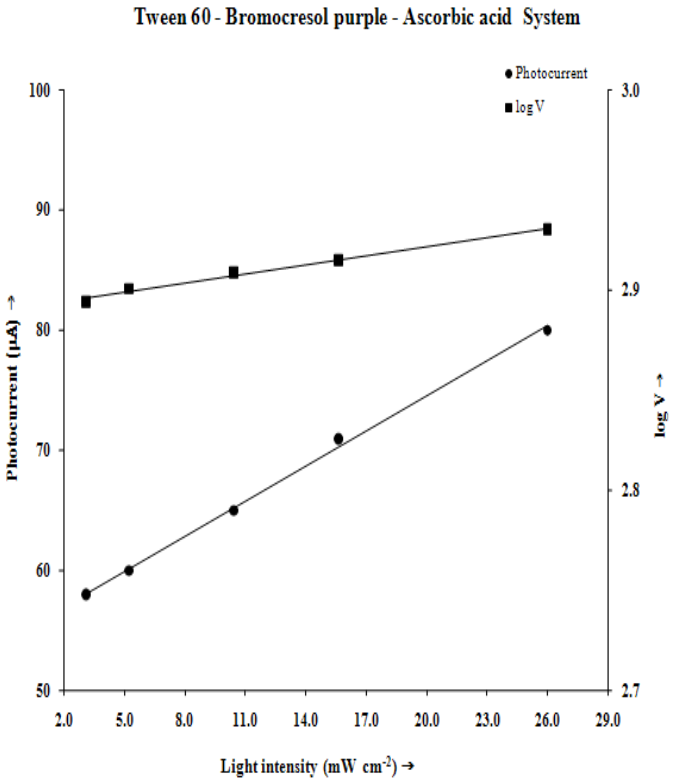


Fig. 1 Variation of photocurrent and photopotential (log V) with light intensity

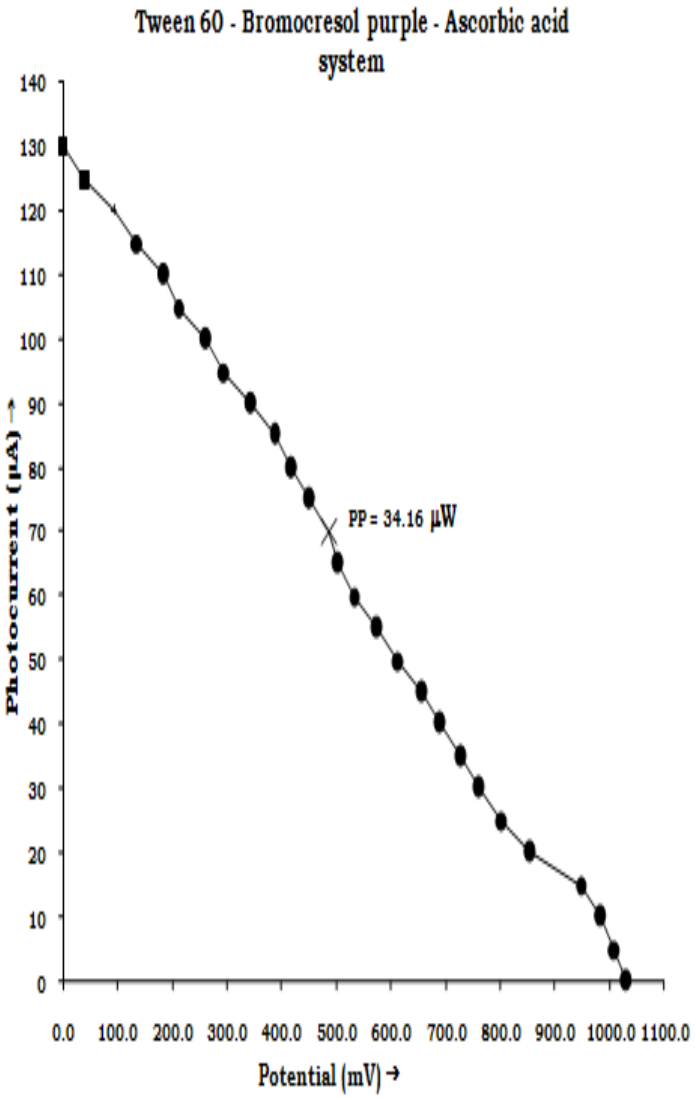


Fig. 2 Current - potential (i-V) curve of the cell

Bromocresol purple - Tween 60 combination of concentration 1.6×10^{-5} M + 1.2×10^{-3} M. The changes in the spectra can be seen in the Fig.4.

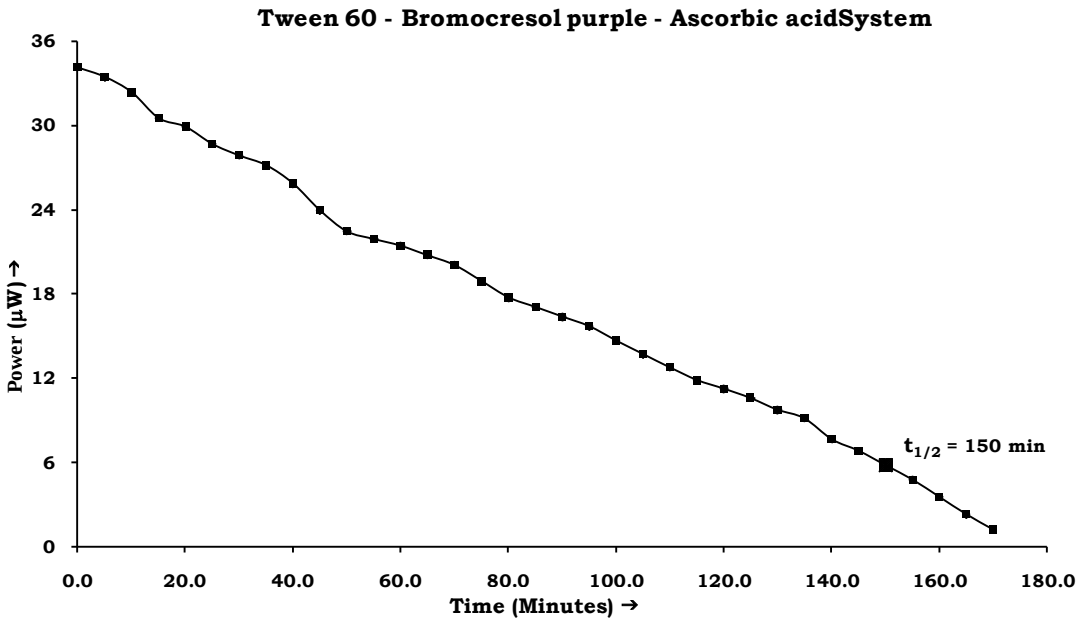


Fig. 3 Time - power curve of the cell

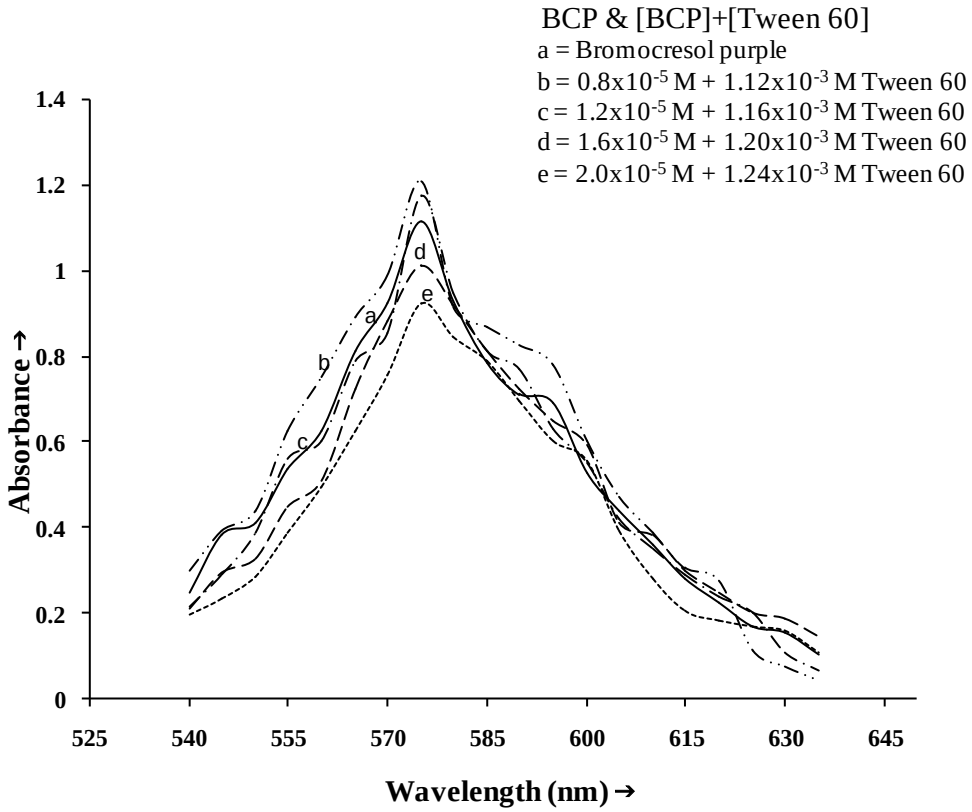


Fig. 4 Absorption spectrum of dye and Dye + surfactant combinations

TableI EFFECT OF VARIATION OF BROMOCRESOL PURPLE, TWEEN 60, ASCORBIC ACID CONCENTRATION.

Concentration	**Photo potential (mV)**	**Photocurrent (μA)**
[Bromocresol purple] x 10^{-5} M		
0.8	740	38
1.2	768	53
1.6	811	65
2.0	763	54
2.4	731	47
[Tween 60] x 10^{-3} M		
1.12	740	26
1.16	784	48
2.00	811	65
1.24	778	46
1.28	736	32
[Asccorbic acid] x 10^{-3} M		
1.92	738	32
1.96	786	56
2.00	811	65
2.04	768	48
2.08	730	29

[a]Light Intensity = 10.4 mW cm^{-2}, [b]Temp. = 303 K, [c]pH = 10.18

TableII EFFECT OF pH

pH	**Photo potential (mV)**	**Photocurrent (μA)**
10.10	772	48
10.14	785	53
10.18	811	65
11.22	798	59
11.26	783	51

[a]Tween 60 = 1.2 x 10^{-3} M, [b]Bromocresol purple = 1.6 x 10^{-5} M, [c]Ascorbic acid = 2.0 x 10^{-3} M, [d]Light Intensity = 10.4 mW cm^{-2}, [e]Temp. = 303 K

TableIII EFFECT OF DIFFUSION LENGTH

Diffusion length D_L(mm)	**Maximum photocurrent i_{max}(μA)**
50	117
55	124
60	130
65	135
70	140

[a]Tween 60 = 1.2 x 10^{-3} M, [b]Bromocresol purple = 1.6 x 10^{-5} M, [c]Ascorbic acid = 2.0 x 10^{-3} M, [d]Light Intensity = 10.4 mW cm^{-2}, [e]Temp. = 303 K, fpH = 10.18

TableIV EFFECT OF ELECTRODE AREA

Tween 60 – Bromocresol purple - Ascorbic acid System	Electrode area (cm^2)				
	0.25	0.64	1.00	1.21	1.96
Maximum photocurrent i_{max} (μA)	117	121	130	136	141
Equilibrium photocurrent I_{eq} (μA)	58	62	65	72	81

[a]Tween 60 = 1.2 x 10^{-3} M, [b]Bromocresol purple = 1.6 x 10^{-5} M, [c]Ascorbic acid 2.0 x 10^{-3} M, [d]Light Intensity = 10.4 mW cm^{-2}, [e]Temp. = 303 K, fpH = 10.18

CONCLUSIONS

Fossil fuels meet our energy more chirpy than solar alternatives, in part because fossil fuels deposit are concentrated source of energy, whereas the sun distributes photons fairly uniformly over earth at a more modest energy density. The cost and capacity limited on solar energy use are most effectively addressed by a single research objective cost effectively raising conversion efficiency. The enormous gap between the potential of solar energy and our use of it is due cost and conversion capacity. On the basis of result obtained in the present photogalvanic cell system Tween 60 – Bromocresol purple – Ascorbic acid system, it may be concluded that value of conversion efficiency, storage capacity and fill factor observed are reasonable and this system can be used in photogalvanic cell for solar energy conversion and storage device.

ACKNOWLEDGEMENTS

The authors are thankful UGC, New Delhi for providing financial assistance under UGC Major Research Project (No. 40-55/2011 (SR) dated 5 July 2011).

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